

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01F 1/057, C22C 38/00		A1	(11) International Publication Number: WO 99/21196 (43) International Publication Date: 29 April 1999 (29.04.99)
(21) International Application Number: PCT/US98/21884		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 16 October 1998 (16.10.98)			
(30) Priority Data:			
60/062,940	22 October 1997 (22.10.97)	US	
60/062,939	22 October 1997 (22.10.97)	US	
60/062,830	22 October 1997 (22.10.97)	US	
60/062,832	22 October 1997 (22.10.97)	US	
09/001,727	31 December 1997 (31.12.97)	US	
(71) Applicant (for all designated States except US): RHODIA INC. [US/US]; 259 Prospect Plains Road, Cranbury, NJ 08512 (US).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): MA, Bao-Min [US/US]; 8 Hamton Court East, Robbinsville, NJ 08691 (US). BOUNDS, Charles, O. [US/US]; 22 Beechwood Lane, Yardley, PA 19067 (US). CHANG, Wen, Cheng [-]; 5F2, No. 43, Lane 495, Sec. 2, Da Ya Road, Chia-Yi (TW). CHEN, Qun [CN/CN]; 305 Trinity Court #11, Princeton, NJ 08540 (US).			
(74) Agent: CARLETON, Katherine, L.; 259 Prospect Plains Road, Cranbury, NJ 08512 (US).			
<p style="text-align: center;"><i>Ser</i></p> <p style="text-align: right;"><i>4,322,933</i></p>			

(54) Title: IRON-RARE EARTH-BORON-REFRACTORY METAL MAGNETIC NANOCOMPOSITES

(57) Abstract

Magnetic nanocomposite materials including iron, rare earth elements, boron, refractory metal and, optionally, cobalt are disclosed. Neodymium and lanthanum are preferred rare earth elements. The amounts of Nd, La, B and refractory metal are controlled in order to produce both hard and soft magnetic phases, as well as a refractory metal boride precipitated phase. The refractory metal boride precipitates serve as grain refiners and substantially improve the magnetic properties of the nanocomposite materials. The materials are particularly suitable for making bonded magnets.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

IRON-RARE EARTH-BORON-REFRACTORY METAL MAGNETIC NANOCOMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of United States Provisional Application Serial Nos. 60/062,830, 60/062,832, 60/062,939 and 60/062,940, filed October 22, 1997, each of which is incorporated herein by reference.

5

FIELD OF THE INVENTION

The present invention relates to magnetic materials, and more particularly relates to magnetic nanocomposite materials including iron, rare earth elements, boron and refractory metals which have favorable magnetic properties and are suitable for making bonded magnets.

10

BACKGROUND INFORMATION

Magnetic alloys containing neodymium, iron and boron have been widely studied for use in sintered and bonded magnets due to their favorable magnetic properties. The Nd₂Fe₁₄B phase has been identified as a hard magnetic phase exhibiting particularly good magnetic properties.

15

U.S. Patent Nos. 4,402,770, 4,409,043 and Re. 34,322 to Koon, which are incorporated herein by reference, disclose magnetic alloys comprising lanthanum and other rare earth elements, transition metals such as iron and cobalt, and boron within specified ranges. Although the disclosed alloys have been found to possess good magnetic properties, such alloys do not have optimal properties, and have not become commercially viable.

20

The present invention has been developed in view of the foregoing and to address other deficiencies of the prior art.

SUMMARY OF THE INVENTION

The present invention provides a nanocomposite magnetic material of controlled composition which exhibits improved magnetic properties and can be easily processed.

5 An object of the present invention is to provide a nanocomposite magnetic material comprising Fe, rare earth elements, B, refractory metals and, optionally, Co within specified ranges.

10 Another object of the present invention is to provide a nanocomposite magnetic material of the formula: $(Nd_{1-y}La_y)_v Fe_{100-v-w-x-z}Co_wM_zB_x$, where M is at least one refractory metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.05 to about 0.5; and z is from about 0.1 to about 5.

15 A further object of the present invention is to provide a nanocomposite magnetic material including a hard magnetic phase, a soft magnetic phase, and a refractory metal boride precipitated phase. The hard magnetic phase is preferably $Nd_2Fe_{14}B$, while the soft magnetic phase preferably comprises α -Fe, Fe₃B or a combination thereof.

20 Another object of the present invention is to provide a method of making a nanocomposite magnetic material. The method includes the steps of providing a molten composition comprising Fe, rare earth elements, B, at least one refractory metal and, optionally, Co, rapidly solidifying the composition to form a substantially amorphous material, and thermally treating the material to form crystalline magnetic phases of desired composition and size.

25 These and other objects of the present invention will become more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ternary phase diagram showing the total rare earth (TRE), iron/cobalt (Fe, Co), and boron (B) content of nanocomposite magnetic materials in accordance with an embodiment of the present invention.

30 Fig. 2 is a series of X-ray diffraction patterns for rapidly solidified compositions comprising Nd, Fe and varying amounts of B, showing a change from crystalline to amorphous microstructure when the amount of B is increased.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The magnetic nanocomposite compositions of the present invention include rare earth elements, iron, boron, refractory metals and, optionally, cobalt. Suitable rare earth elements include La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. The total rare earth content of the present compositions is referred to herein as "TRE". The term "RE" as used herein means all of the suitable rare earth elements except La. Preferred RE elements are Nd, Pr, Dy; Tb and mixtures thereof, with Nd, Pr and mixtures thereof being most preferred. Suitable refractory metals include elements of Groups IVb, Vb and VIb of the Periodic Table, e.g., Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. The refractory metal content of the present compositions is referred to herein as "M". Typical, preferred and more preferred ranges of TRE, B, M and Co are set forth in Table 1.

Table 1

Compositions (atomic percent)

	TRE	B	M	Co	Fe
typical	5-15	9-30	0.1-5	0-40	balance
preferred	9-12	9-12	0.5-3	1-20	balance
more preferred	9.5-11.5	9.5-11	1-2.5	5-15	balance

In accordance with the present invention, the compositions of the present invention may correspond to the formula: $(RE_{1-y}La_y)_v Fe_{100-v-w-x-z} Co_w M_x B_z$, where RE is at least one rare earth element excluding La; M is at least one refractory metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.05 to about 0.5; and z is from about 0.1 to about 5. Preferably, RE is at least one element selected from Nd, Pr, Dy and Tb; M is at least one refractory metal selected from Ti, V, Nb, Cr and Mo; v is from about 9 to about 12; w is from about 1 to about 20; x is from about 9 to about 12; y is from about 0.05 to about 0.1; and z is from about 0.5 to about 3. More preferably, RE is Nd, Pr or a mixture thereof; M is Ti, Nb or Cr; v is from about 9.5 to about 11.5; w is from about 5 to about 15; x is from about 9.5 to about 11; y is from about 0.05 to

about 0.1; and z is from about 1 to about 2.5. In particularly preferred compositions, v is about 11.0, w is about 10, x is about 10.5, y is about 0.05 or 0.075, and z is about 2.

Alternatively, the compositions of the present invention may be expressed by the formula: $(Fe_wM_xB_{1-w-x})_{1-y}(R_zLa_{1-z-y})_y$, where M is at least one refractory metal selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; R is at least one rare earth element selected from Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, By and Lu; w is from about 0.7 to about 0.9; x is from about 0.001 to about 0.06; y is from about 0.05 to about 0.15; z is from about 0.5 to about 0.95; and up to about 40 atomic percent of the Fe may optionally be replaced by Co. This alternative nomenclature is similar to the nomenclature used in U.S. Patent No. 4,402,770 to Koon. In accordance with the present invention, the addition of refractory metal within controlled amounts to compositions similar to those disclosed in U.S. Patent No. 4,402,770 to Koon has been found to substantially improve the properties of the compositions, resulting in a commercially viable magnetic nanocomposite material.

The TRE content of the present compositions is controlled in order to provide desirable properties. Neodymium is a preferred rare earth element, which is provided in sufficient amounts to form the desired molar fraction of the $Nd_2Fe_{14}B$ hard magnetic phase. Some or all of the Nd may be substituted by Pr. The TRE constituent preferably includes a minor amount of La which provides several benefits. For example, La is a glass former which facilitates the formation of an amorphous precursor alloy by rapid solidification. Furthermore, La has been found to suppress grain growth during subsequent thermal treatment of the rapidly solidified amorphous alloy. Lanthanum preferably comprises from about 5 to about 50 atomic percent of the total rare earth content of the compositions.

The B content of the present compositions is controlled in order to form the desired amount of the hard magnetic phase (e.g., $Nd_2Fe_{14}B$), and to form borides of the refractory metal constituent of the compositions. As described more fully below, such borides act as a precipitation hardening or grain refining phase which improves the properties of the compositions substantially. Furthermore, B is a glass former which facilitates formation of an amorphous product during rapid solidification of the compositions. A sufficient amount of B should be used in order

to improve the properties of the nanocomposite material. Boron levels of greater than or equal to about 9 or 9.5 atomic percent are preferred, with levels of greater than or equal to about 10 or 10.5 atomic percent being particularly preferred.

5 The refractory metal M content of the present compositions is controlled in order to provide grain refinement of the compositions, while avoiding substantial degradation of magnetic properties. At least a portion of the refractory metal reacts with boron to form borides, which promote homogenous nucleation of magnetic phase grains. The refractory borides are located, at least in part, at the grain boundaries of the magnetic phases, and produce grain refinement thereof. In
10 addition, the refractory metal borides suppress formation of the undesirable $Nd_2Fe_{23}B$, metastable phase, and promote the formation of the $Nd_2Fe_{14}B$ and α -Fe magnetic phases. However, at too high a concentration, the refractory metal may react to an undesirable extent with boron to form large particles which are located at the triple junctions between grains of the magnetic phases. Furthermore, if too
15 much of the refractory metal is present it will preferentially react with boron, thereby suppressing the formation of the desirable $Nd_2Fe_{14}B$ hard magnetic phase.

20 Cobalt may be added to the present compositions in order to increase remanence and maximum energy product magnetic properties. Cobalt additions may also increase the Curie temperature (T_c) of the hard magnetic phase and increase the fluidity of the molten alloy.

25 The nanocomposite materials of the present invention preferably comprise a hard magnetic phase, a soft magnetic phase, and a refractory metal boride precipitated phase. The hard magnetic phase comprises $RE_2Fe_{14}B$, while the soft magnetic phase may include α -Fe, α -(Fe,Co), Fe₃B, (Fe,Co)₃B, Fe₂B and (Fe,Co)₂B. Typically, the hard magnetic phase comprises $Nd_2Fe_{14}B$ and the soft magnetic phase comprises α -Fe, Fe₃B or a combination thereof. The refractory metal boride precipitated phase may comprise borides such as TiB, Ti₃B₄, TiB₂, NbB₂, NbB, Nb₃B₂, CrB, CrB₂, Cr₃B₄, Mo₂B, MoB, Mo₂B₃, MoB₄, ZrB₂, W₂B, WB, W₂B₅, WB₅, VB, V₃B₄, VB₂ and combinations thereof. The average size of
30 the refractory metal precipitates is typically from about 1 to about 30 nanometers. The refractory metal boride precipitate provides nucleation sites and acts as a grain refiner which improves the magnetic properties of the compositions substantially.

Phases which degrade magnetic properties to an undesirable extent are preferably minimized or eliminated from the compositions. For example, the RE₂Fe₂₃B₃ (e.g., Nd₂Fe₂₃B₃) metastable phase is preferably reduced or eliminated. Other phases such as Nd-Fe eutectic, Nd₂Fe₁₇, Nd₂Co₁₇ and NdFe₄B₄ may also be reduced or eliminated from the compositions. In accordance with the present invention, the incorporation of refractory metal and the resultant formation of the refractory metal boride precipitated phase has been found to suppress the formation of the Nd₂Fe₂₃B₃ metastable phase. Prior to the present invention, alloy compositions with amounts of boron above about 9 or 10 atomic percent and rare earth amounts of about 7 to about 11.7 atomic percent have not been studied in depth and reported in the open literature because of the formation of undesirable phases, such as Nd₂Fe₂₃B₃, and the difficulty of obtaining materials with sufficiently high intrinsic coercivity (H_c) when soft magnetic materials are present.

The nanocomposite materials of the present invention are preferably in powder form, having preferred average particle sizes of from about 10 to about 200 microns. The powders are preferably magnetically isotropic, and possess favorable magnetic properties such as remanence (B_r), intrinsic coercivity (H_c) and/or maximum energy product (BH_{max}). The materials preferably have a B_r of greater than about 7.2 kG, H_c of greater than about 6.0 kOe, and BH_{max} of greater than about 8.0 MGoe.

While not intending to be bound by any particular theory, the nanocomposite materials of the present invention are believed to exhibit exchange coupling which results from the combination of hard and soft magnetic phases having controlled sizes and desired distribution. As used herein, the term "exchange coupling" means the electron exchange interaction coupled between the hard and soft magnetic phases. The average grain size of the soft magnetic phase is preferably less than the domain wall width of the hard magnetic phase (e.g., Nd₂Fe₁₄B). The average grain size of the soft magnetic phase is preferably from about 2 to about 60 nanometers, while the average grain size of the hard magnetic phase is from about 10 to about 100 nanometers. More preferably, the soft magnetic phase has an average grain size of from about 2 to about 30 nanometers, while the hard magnetic phase has an average grain size of from about 10 to about 50 nanometers. For effective exchange coupling to occur the average grain size of

the soft magnetic phase should preferably be no larger than the domain wall width of the hard magnetic phase, which has been estimated to be from about 10 to about 30 nanometers for the hard magnetic phase Nd₂Fe₁₄B.

5 In accordance with the present invention, the grain sizes of the soft and hard magnetic phases are controlled by the refractory metal boride precipitated phase, as well as the thermal processing conditions. The grain refining effect of the refractory metal boride precipitate phase promotes exchange coupling, and substantially improves the magnetic properties and processibility of the nanocomposite materials.

10 The magnetic materials of the present invention are preferably produced by a rapid solidification and thermal treatment process. Rapid solidification is achieved by quickly cooling the composition from the molten state by techniques such as melt spinning, jet casting, melt extraction, atomization and splat cooling. Cooling rates of from about 10⁴ to about 10⁷°C per second are typically employed, preferably from about 10⁵ to about 10⁶°C per second. The rapidly solidified material is preferably substantially amorphous. After rapid solidification the material may be ground, may be ground and heat treated, or may be directly heat treated.

15 20 The compositions of the present invention have been found to possess improved processibility, allowing slower rapid solidification rates to be used. For example, during the melt spinning process, slower rotational wheel speeds may be used and/or larger volumes of material may be processed. The ability to use slower melt spinning wheel speeds is important because the molten alloy puddle that is in contact with the spinning wheel is substantially more stable when the wheel speed is reduced. Furthermore, the ability to process larger volumes of material allows for reductions in production costs.

25 30 After the composition has been rapidly solidified to the substantially amorphous state, it is preferably thermally treated to induce spontaneous crystallization. As used herein, the term "spontaneous crystallization" means the rapid and substantially homogenous formation of fine crystal grains. In accordance with the present invention, the refractory metal boride phase acts as a grain refiner. The boride phase is also believed to provide nucleation sites for the soft and hard

magnetic phases. These phases nucleate, but do not exhibit substantial grain growth after they nucleate.

Spontaneous crystallization is preferably achieved by heating the material to a specified temperature for a controlled period of time, which results in nucleation of crystal grains without substantial subsequent grain growth. Temperatures of from about 400 to about 800°C are suitable, preferably from about 650 to about 750°C. Heating times of from about 0.001 second to about 2 hours are preferred, more preferably from about 0.01 second to about 10 minutes. The material may be heated in any suitable apparatus such as a furnace. Continuous and/or batch heating methods may be employed. Preferably, the material is heated to its crystallization temperature and the heat source is removed before substantial grain growth occurs.

The following examples illustrate various aspects of the present invention and are not intended to limit the scope thereof.

Example 1

Alloy ingots of $\text{Nd}_{9.5}\text{Fe}_{85.5-x}\text{B}_x$, where $x = 5, 6, 7, 8, 9, 10$ and 10.5, are prepared by vacuum induction melting. A laboratory jet caster with a Cu-wheel is used for melt spinning. A wheel speed of 15-30 m/sec is used for preparing samples. The crystallization temperatures are determined by a Perkin-Elmer Differential Thermal Analyzer (DTA-7). A Siemens x-ray diffractometer is used to determine the degree of amorphousness of the as-spun materials. Fig. 2 shows the x-ray diffraction patterns of $\text{Nd}_{9.5}\text{Fe}_{85.5-x}\text{B}_x$ melt spun at a wheel speed of 18 m/sec., where $x = 10.5$ (pattern a), $x = 9$ (pattern b), $x = 7$ (pattern c), and $x = 5$ (pattern d). As can be seen, at $x < 9$, materials obtained are partially crystallized in the as-melt spun state. Both α -Fe and $\text{Nd}_2\text{Fe}_{14}\text{B}$ are present. The amount of α -Fe decreases with the increasing B-content. At $x > 9.5$, these materials are nearly amorphous and α -Fe is diminished. Table 2 lists the optimum magnetic properties after thermal treatment. In general, H_{ci} decreases with increasing boron content up to about 9 atomic percent, and then increases with boron levels above about 9 atomic percent. A similar trend can also be observed for B_r and BH_{max} . This indicates that there is a change in either the phase formation/distribution or the magnetization mechanism when the boron content is increased above about 9 atomic

percent. These data show that in Nd-Fe-B alloys incremental increases in the boron content above approximately 6 atomic percent lead to a steady decrease in the magnetic properties (e.g., B_r and H_{ci}) of the coercive powder and provides a possible explanation why such alloys have not been utilized commercially.

5

Table 2

B Content (x)	T_g ($^{\circ}$ C)	B_r (kG)	H_{ci} (kOe)	BH_{max} (kOe)
5	crystallized	11.7	6.6	18.7
6	650	11.9	6.3	19.0
8	710	9.5	5.2	13.5
9		8.0	4.5	9.4
10		8.0	4.9	9.8
10.5		8.4	5.1	11.0

Example 2

Alloy ingots of $(Nd_{1-y}La_y)_{9.5}Fe_{85.5}B_5$, where $y=0, 0.05, 0.10$ or 0.15 atomic percent, are prepared by vacuum induction melting. A laboratory jet caster with a Cu-wheel is used for melt spinning. A wheel speed of about 15-20 m/sec is used for preparing samples. The crystallization temperatures are determined by a Perkin-Elmer Differential Thermal Analyzer (DTA-7). Melt spun ribbons are thermal treated in a temperature range of 650 to 670° C for 10 minutes. The magnetic properties obtained after optimum thermal treatment are listed in Table 3. The crystallization temperature decreases from 569 to 562° C when the La content increases from 0 to 0.15 atomic percent. Considerable increases in both B_r and BH_{max} are observed in materials with some La substitution for Nd. These data show that the substitution of La for Nd in certain alloy compositions shows some improvement, e.g., increases the B_r with only minor reduction in H_{ci} .

Table 3

La Content (y)	T _g (°C)	B _r (kG)	H _{ci} (kOe)	BH _{max} (kOe)
5	0	569	8.6	11.0
	0.05	564	9.6	13.5
	0.10	563	9.8	12.5
	0.15	562	9.2	12.0

Example 3

Alloy ingots of $(Nd_{0.95}La_{0.05})_{9.5}Fe_{81.5-z}Cr_zB_9$ are prepared by vacuum induction melting. A laboratory jet caster with a Cu-wheel is used for melt spinning. A wheel speed of 15-18 m/sec is used for preparing the $(Nd_{0.95}La_{0.05})_{9.5}Fe_{81.5-z}Cr_zB_9$ samples. The crystallization temperatures are determined by a Perkin-Elmer Differential Thermal Analyzer (DTA-7). Melt spun ribbons are thermally processed in the temperature range of 650 to 670°C for 10 minutes. The magnetic properties obtained after optimum thermal treatment are listed in Table 4.

10 The Cr substitution increases the crystallization temperature from 608 to 635°C when the Cr content increases from 0 to 8.1 atomic percent. Because of the diluting effect, the B_r decreases with increasing Cr content. A significant increase in H_{ci} is observed when the Cr content is increased from 0 to 2.7 atomic percent. These data show that the H_{ci} of the magnetic powder of certain compositions can be increased by the substitution of a Cr refractory metal for Fe, with only a minor decrease in the B_r.

15

20

Table 4

Cr Content (z)	T _g (°C)	B _r (kG)	H _{ci} (kOe)	BH _{max} (kOe)
25	0	9.8	6.1	11.5
	2.7	8.3	9.0	12.3
	5.4	8.0	9.2	11.8
	8.1	6.7	9.8	7.7

Example 4

Alloy ingots of $(Nd_{0.95}La_{0.05})_vFe_{88-v}Cr_2B_{10}$, where $v = 7.5$ to 11.5 , are prepared by vacuum induction melting. A laboratory jet caster with Cu-wheel is used for melt spinning. A wheel speed in the range of 15 to 25 m/sec is used for melt spinning. The melt spun ribbons obtained are thermally processed in the temperature range of 675 to $700^\circ C$ for 10 minutes. The optimum magnetic properties are listed in Table 5. These data illustrate the effect of varying amounts of TRE in alloys containing 10 atomic percent B. The preferred alloys are in the range of from about 9.5 to about 11.5 atomic percent TRE.

10

Table 5

v	B_r (kG)	H_{ci} (kOe)	BH_{max} (MGOe)
7.5	8.5	3.1	8.1
8.5	8.3	4.0	10.0
9.5	8.6	9.1	12.6
10.5	9.2	11.1	16.5
11.0	9.5	13.2	18.0
11.5	9.9	5.0	14.0

Example 5

Alloy ingots of $(Nd_{0.95}La_{0.05})_{9.5}Fe_{88-w}Co_wCr_2B_{10.5}$, where $w = 0$ to 10 atomic percent, are prepared by vacuum induction melting. A laboratory jet caster with Cu-wheel is used for melt spinning. A wheel speed in range of 15 to 25 m/sec is used for melt spinning. Melt spun ribbons obtained are thermally processed in the temperature range of 675 to $700^\circ C$ for 10 minutes. The optimum magnetic properties are listed in Table 6. The substitution of Co for Fe causes a dramatic increase in the B_r , with only a minor decrease in the H_{ci} , for alloy powders that contain La substituted for Nd and a refractory metal.

25

21

Table 6

Co Content (w)	B _r (kG)	H _{ci} (kOe)	BH _{max} (MGOe)
0 and without Cr	7.8	6.2	9.5
0	8.4	10.3	14.0
2.5	8.4	10.2	14.1
5.0	8.5	10.2	14.1 ..
7.5	9.1	10.3	15.8
10.0	10.0	9.5	19.8

Example 6

Alloy ingots of $(Nd_{0.95}La_{0.05})_{9.5}Fe_{78}M_1B_{10.5}$, where M = Cr, Ti, V, Mo or Nb, are prepared by vacuum induction melting. A comparative composition containing no refractory metal addition corresponding to a composition with the ranges disclosed in U.S. Patent No. 4,402,770 to Koon is prepared in an identical manner. A laboratory jet caster with Cu-wheel is used for melt spinning. A wheel speed in range of 15 to 25 m/sec is used for melt spinning. Melt spun ribbons obtained are thermally processed in the temperature range of 650 to 700°C for 10 minutes. The optimum magnetic properties obtained are listed in Table 7. These data establish that Cr, Ti, V, Mo and Nb refractory metal additions substantially improve magnetic properties in accordance with a preferred embodiment of the present invention.

Table 7

M	B _r (kG)	H _{ci} (kOe)	BH _{max} (MGOe)
no addition	7.8	6.2	9.5
Cr	8.3	14.1	13.9
Ti	8.8	11.9	15.0
V	8.7	9.6	15.0
Mo	8.3	10.5	14.0
Nb	8.0	14.1	13.0

Example 7

Compositions of the formula $(Nd_{0.95}La_{0.05})_{10.5}Fe_{67}Co_{10}M_2B_{10.5}$ are prepared as in the previous example, wherein M = Ti, Nb, Cr, Hf, W and Zr. A comparative composition containing no refractory metal addition corresponding to a composition with the ranges disclosed in U.S. Patent No. 4,402,770 to Koon is prepared in an identical manner. The magnetic properties of the resultant compositions are listed in Table 8. Compositions in accordance with the present invention containing Co in combination with refractory metal additions exhibit substantially increased H_{ci} and BH_{max} properties.

10

Table 8

M	B_r (kG)	H_{ci} (kOe)	BH_{max} (MGoe)
no addition	7.8	6.3	9.8
Ti	9.5	15.4	18.2
Nb	8.8	19.4	16.2
Cr	9.8	12.6	18.8
Hf	9.7	10.4	19.8
W	9.6	15.2	18.6
Zr	9.5	14.0	17.5

15

20

25

Conventional magnetic alloy compositions are listed below in Table 9. The composition labelled "MQ" is commercially available from Magnequench International under the designation MQP-B, while the composition labelled "SSM" is commercially available from Sumitomo Special Metals Co. under the designation NEOMAX. These commercially available compositions have relatively high levels of rare earth elements and relatively low levels of B in comparison with the preferred compositions of the present invention.

Table 9

Composition	TRE	TM atomic percent	B
Nd ₂ Fe ₁₄ B	11.7	balance	6.0
MQ	12.2-13.7	balance	5.7-5.8
SSM	14.0-15.0	balance	6.0-8.0

5

Table 10 lists the phases in molar fraction percent of conventional alloy compositions of the formula Nd_{13.7}Fe_{80.7}B_{5.6} (MQP-A) and of the formula Nd_{12.2}Fe_{77.0}Co_{5.0}B_{5.8} (MQP-B), in comparison with compositions of the present invention having compositions of the formula (Nd_{0.95}La_{0.05})_{11.0}Fe_{73.3}Co_{5.2}B_{10.5} (Comp. No. 1) and of the formula (Nd_{0.95}La_{0.05})_{9.5}Fe₇₅Co₅B_{10.5} (Comp. No. 2). The MQP-A and MQP-B compositions are commercially available from Magnequench International.

10

Table 10

15

Phases	MQP-A	MQP-B	Comp. No. 1	Comp. No. 2
Nd ₂ Fe ₁₄ B	96	98	74	72
α-Fe	0	0	1	5-7
Fe ₃ B	---	---	22-24.7	20
Nd _{1.1} Fe ₄ B ₄	0.01-0.1	0.08-0.2	0.3-3	1-3
Nd-Fe eutectic	4	1.8°	0	0

20

25

In accordance with the present invention, bonded magnets with superior performance can be produced from the rapidly solidified and thermally processed coercive nanocomposite powders made from the compositions of the present invention. The bonded magnets may comprise, for example, from about 0.5 to about 4 weight percent of a binder of any suitable composition such as epoxy, nylon 6-6, polypropylene (PPE) or low melting point metals. The bonded magnets may be prepared by any suitable method. For example, the alloy may be ground to a powder having an average particle size of about 200 microns. The powder is combined and mixed with epoxy in a proportion of about 98 weight percent

5

powder and about 2 weight percent epoxy. The materials are mixed by hand. The mixture is then placed into a die (about 10mm) and pressed with a pressure of about 7.5 MT/cm² for approximately 30 seconds. The resulting pellet is released from the mold and cured at about 175°C for approximately one hour. The pellet is then removed and allowed to cool to room temperature. The appropriate measurements of density and magnetic properties are then performed.

10

Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

WHAT IS CLAIMED IS:

1. A nanocomposite magnetic material of the formula:
 $(RE_{1-y}La_y)_v Fe_{100-v-w-x-z}Co_wM_zB_x$, where RE is at least one element selected from the group consisting of Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; M is at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.05 to about 0.5; and z is from about 0.1 to about 5.
2. The nanocomposite material of Claim 1, wherein RE is at least one element selected from the group consisting of Nd, Pr, Dy and Tb.
3. The nanocomposite material of Claim 1, wherein RE is at least one element selected from the group consisting of Nd and Pr.
4. The nanocomposite material of Claim 3, wherein M is at least one refractory metal selected from the group consisting of Ti, V, Nb, Cr and Mo; v is from about 9 to about 12; w is from about 1 to about 20; x is from about 9 to about 12; y is from about 0.05 to about 0.1; and z is from about 0.5 to about 3.
5. The nanocomposite material of Claim 3, wherein M is at least one refractory metal selected from the group consisting of Ti, Nb or Cr; v is from about 9.5 to about 11.5; w is from about 5 to about 15; x is from about 9.5 to about 11; y is from about 0.05 to about 0.07; and z is from about 1 to about 2.5.
6. The nanocomposite material of Claim 3, wherein x is greater than or equal to about 9.5.
7. The nanocomposite material of Claim 3, wherein x is greater than or equal to about 10.

8. The nanocomposite material of Claim 3, wherein x is greater than or equal to about 10.5.

9. The nanocomposite magnetic material of Claim 3, wherein the material comprises:

- a hard magnetic phase;
- a soft magnetic phase; and
- a refractory metal boride precipitated phase.

10. The nanocomposite magnetic material of Claim 9, wherein the hard magnetic phase comprises $\text{Nd}_2\text{Fe}_{14}\text{B}$ and the soft magnetic phase comprises at least one material selected from the group consisting of $\alpha\text{-Fe}$, $\alpha\text{-(Fe,Co)}$, Fe_3B , $(\text{Fe,Co})_3\text{B}$, Fe_2B and $(\text{Fe,Co})_2\text{B}$.

11. The nanocomposite magnetic material of Claim 10, wherein the soft magnetic phase comprises $\alpha\text{-Fe}$, Fe_3B or a combination thereof.

12. The nanocomposite magnetic material of Claim 9, wherein the material is substantially free of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$.

13. The nanocomposite magnetic material of Claim 9, wherein the hard magnetic phase has an average grain size of from about 10 to about 100 nanometers, and the soft magnetic phase has an average grain size of from about 2 to about 60 nanometers.

14. The nanocomposite magnetic material of Claim 13, wherein the refractory metal boride precipitated phase has an average size of from about 1 to about 30 nanometers.

15. The nanocomposite magnetic material of Claim 3, wherein the material is in powder form.

16. The nanocomposite magnetic material of Claim 15, wherein the powder has an average particle size of from about 10 to about 200 microns.

17. The nanocomposite magnetic material of Claim 15, wherein the powder is rapidly solidified and heat treated.

18. The nanocomposite magnetic material of Claim 15, wherein the powder is substantially magnetically isotropic.

19. A nanocomposite magnetic material comprising:
Fe;
from about 5 to about 15 atomic percent total rare earth elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, wherein La comprises at least about 5 atomic percent of the total rare earth elements, and the remainder of the rare earth elements comprise at least about 50 atomic percent Nd, Pr or a combination thereof;
from about 9 to about 30 atomic percent B;
at least about 0.1 atomic percent of at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; and
from 0 to about 40 atomic percent Co.
20. The nanocomposite magnetic material of Claim 19, wherein the total rare earth elements comprise from about 9 to about 12 atomic percent, the B comprises from about 9 to about 12 atomic percent, the refractory metal comprises from about 0.5 to about 3 atomic percent, the Co comprises from about 1 to about 20 atomic percent.
21. The nanocomposite magnetic material of Claim 19, wherein the total rare earth elements comprise from about 9.5 to about 11.5 atomic percent, the B comprises from about 9.5 to about 11 atomic percent, the refractory metal comprises from about 1 to about 2.5 atomic percent, and the Co comprises from about 5 to about 15 atomic percent.
22. The nanocomposite magnetic material of Claim 19, wherein the La comprises from about 5 to about 50 atomic percent of the total rare earth elements.
23. The nanocomposite magnetic material of Claim 19, wherein the La comprises from about 5 to about 7 atomic percent of the total rare earth elements.
24. The nanocomposite magnetic material of Claim 19, wherein the at least one refractory metal is selected from the group consisting of Ti, V, Nb, Cr and Mo.

25. The nanocomposite magnetic material of Claim 19, wherein the material comprises:

- a hard magnetic phase;
- a soft magnetic phase; and
- a refractory metal boride precipitated phase.

26. The nanocomposite magnetic material of Claim 25, wherein the hard magnetic phase comprises $\text{RE}_2\text{Fe}_{14}\text{B}$ and the soft magnetic phase comprises at least one material selected from the group consisting of α -Fe, α -(Fe,Co), Fe_3B , $(\text{Fe},\text{Co})_3\text{B}$, Fe_2B and $(\text{Fe},\text{Co})_2\text{B}$.

27. The nanocomposite magnetic material of Claim 26, wherein the hard magnetic phase comprises $\text{Nd}_2\text{Fe}_{14}\text{B}$ and soft magnetic phase comprises α -Fe, Fe_3B or a combination thereof.

28. The nanocomposite magnetic material of Claim 25, wherein the material is substantially free of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$.

29. The nanocomposite magnetic material of Claim 25, wherein the hard magnetic phase has an average grain size of from about 10 to about 100 nanometers, and the soft magnetic phase has an average grain size of from about 2 to about 60 nanometers.

30. The nanocomposite magnetic material of Claim 29, wherein the refractory metal boride precipitated phase has an average size of from about 1 to about 30 nanometers.

31. The nanocomposite magnetic material of Claim 19, wherein the material is in powder form.

32. The nanocomposite magnetic material of Claim 31, wherein the powder has an average particle size of from about 10 to about 200 microns.

33. The nanocomposite magnetic material of Claim 31, wherein the powder is rapidly solidified and heat treated.

34. The nanocomposite magnetic material of Claim 31, wherein the powder is substantially magnetically isotropic.

35. A magnetic material comprising a $\text{RE}_2\text{Fe}_{14}\text{B}$ hard magnetic phase, a soft magnetic phase, and a refractory metal boride precipitated phase.

36. The magnetic material of Claim 35, wherein the soft magnetic phase comprises at least one material selected from the group consisting of α -Fe, α -(Fe,Co), Fe_3B , (Fe,Co)₃B, Fe_2B and (Fe,Co)₂B.

37. The nanocomposite magnetic material of Claim 36, wherein the hard magnetic phase comprises $Nd_2Fe_{14}B$ and the soft magnetic phase comprises α -Fe, Fe_3B or a combination thereof.

38. The nanocomposite magnetic material of Claim 36, wherein the material is substantially free of $RE_2Fe_{23}B_3$.

39. The nanocomposite magnetic material of Claim 36, wherein the hard magnetic phase has an average grain size of from about 10 to about 100 nanometers, and the soft magnetic phase has an average grain size of from about 2 to about 60 nanometers.

40. The nanocomposite magnetic material of Claim 39, wherein the refractory metal boride precipitated phase has an average size of from about 1 to about 30 nanometers.

41. The nanocomposite magnetic material of Claim 35, wherein the material is in powder form.

42. The nanocomposite magnetic material of Claim 41, wherein the powder has an average particle size of from about 10 to about 200 microns.

43. The nanocomposite magnetic material of Claim 41, wherein the powder is rapidly solidified and heat treated.

44. The nanocomposite magnetic material of Claim 41, wherein the powder is substantially magnetically isotropic.

45. A method of making a nanocomposite magnetic material comprising:

providing a molten composition comprising:

Fe;

from about 5 to about 15 atomic percent total rare earth elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, wherein La comprises at least about 5 atomic percent of the total rare earth elements, and the remainder of the rare earth elements comprise at least 50 atomic percent Nd, Pr or a combination thereof;

from about 9 to about 30 atomic percent B;

at least about 0.1 atomic percent of at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; and

from 0 to about 40 atomic percent Co;
rapidly solidifying the molten composition to form a substantially amorphous product; and

thermally treating the substantially amorphous product to form the nanocomposite magnetic material.

46. The method of Claim 45, wherein the nanocomposite magnetic material is of the formula: $(RE_{1-y}La_y)_v Fe_{100-v-w-x-z}Co_wM_xB_z$, where RE is at least one element selected from the group consisting of Nd, Pr, Dy and Tb; M is at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.01 to about 0.5; and z is from about 0.1 to about 5.

47. The method of Claim 45, wherein the nanocomposite magnetic material comprises a $RE_2Fe_{14}B$ hard magnetic phase, a soft magnetic phase, and a refractory metal boride precipitated phase.

48. The method of Claim 45, further comprising rapidly solidifying the molten composition at a rate of from about 10^5 to about 10^6 °C per second.

49. The method of Claim 48, further comprising rapidly solidifying the molten composition by melt spinning.

50. The method of Claim 45, further comprising grinding the substantially amorphous product before the thermal treatment thereof.

51. The method of Claim 45, further comprising thermally treating the substantially amorphous product at a sufficient temperature for a sufficient time to cause nucleation of crystalline magnetic phases without substantial grain growth of the nucleated crystalline magnetic phases.

52. A bonded magnet comprising:

a nanocomposite magnetic material of the formula:

$(RE_{1-y}La_y)_v Fe_{100-v-w-x-z}Co_wM_zB_x$, where RE is at least one element selected from the group consisting of Ce, Pr, Nd, Rm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; M is at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.05 to about 0.5; and z is from about 0.1 to about 5; and

a binder.

53. The bonded magnet of Claim 52, wherein the binder comprises from about 0.5 to about 4 weight percent of the bonded magnet.

54. A method of making a bonded magnet comprising:

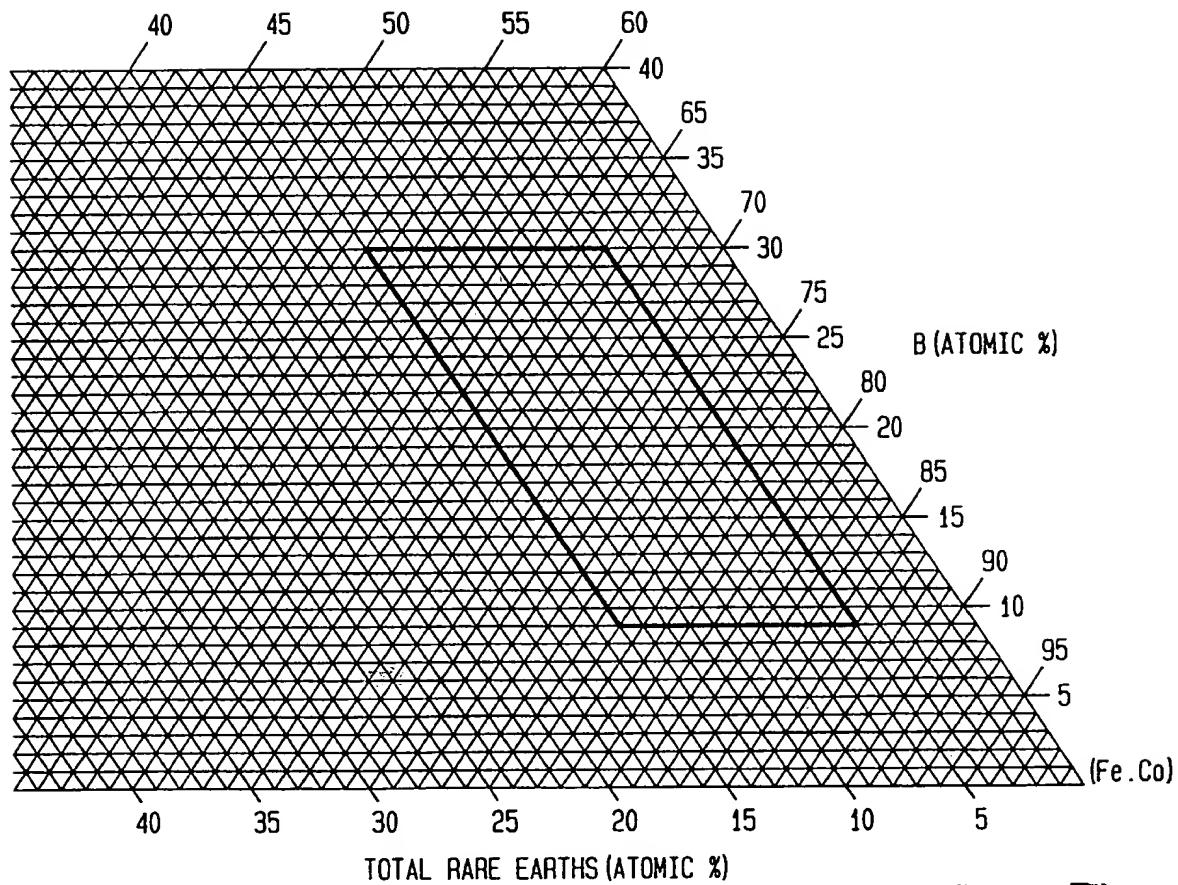
providing a powdered nanocomposite magnetic material of the formula: $(RE_{1-y}La_y)_v Fe_{100-v-w-x-z}Co_wM_zB_x$, where RE is at least one element selected from the group consisting of Ce, Pr, Nd, Rm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; M is at least one refractory metal selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W; v is from about 5 to about 15; w is from 0 to about 40; x is from about 9 to about 30; y is from about 0.05 to about 0.5; and z is from about 0.1 to about 5; and

mixing the powdered nanocomposite magnetic material with a binder; and

curing the binder to form the bonded magnet.

1/2

FIG. 1



SUBSTITUTE SHEET (RULE 26)

2/2
FIG. 2A

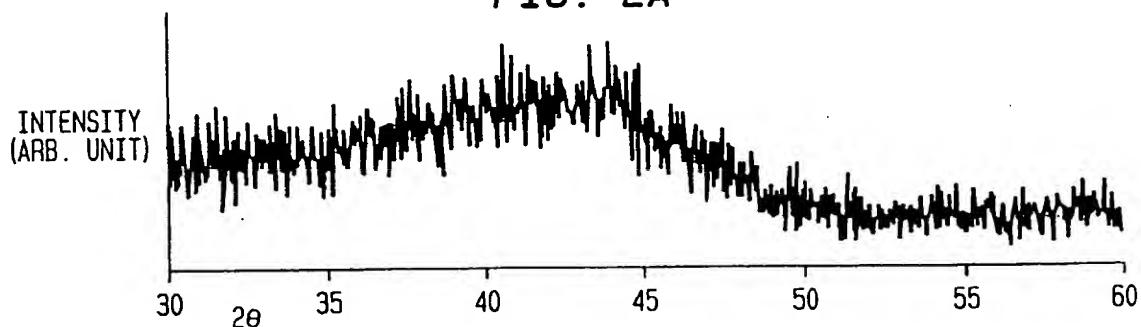


FIG. 2B

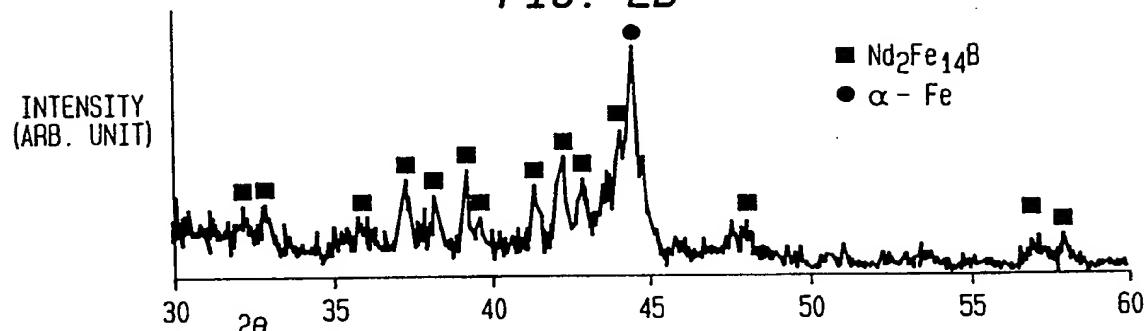


FIG. 2C

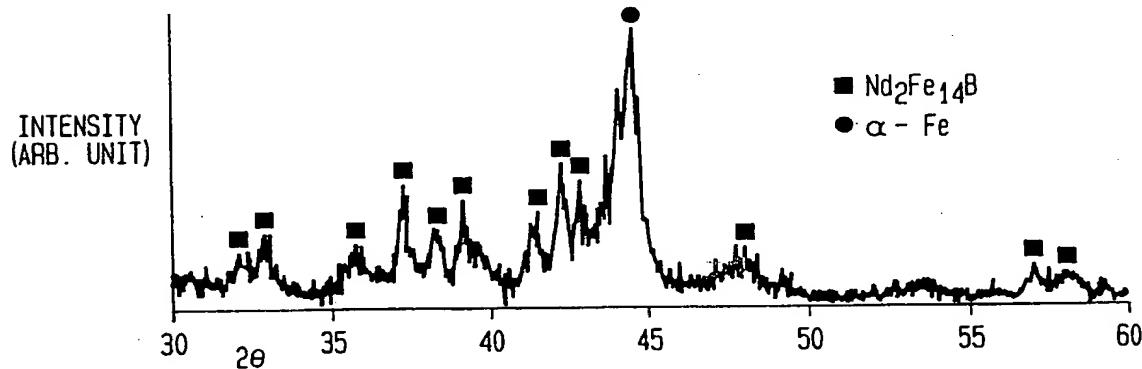
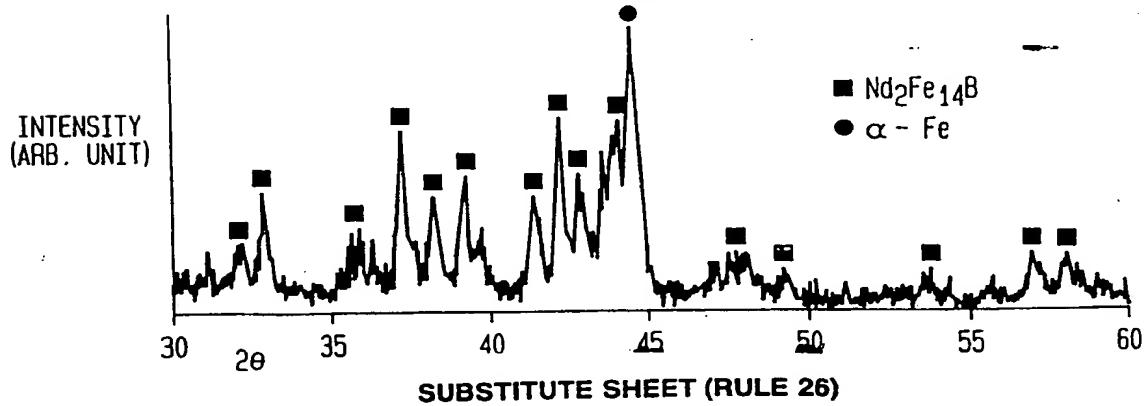


FIG. 2D



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/21884

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01F1/057 C22C38/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01F C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 414 (E-1587), 3 August 1994 & JP 06 124825 A (MITSUBISHI STEEL MFG CO LTD), 6 May 1994 see abstract; example 17 ---	1-8, 19-24
Y	PATENT ABSTRACTS OF JAPAN vol. 097, no. 004, 30 April 1997 & JP 08 335508 A (SUMITOMO SPECIAL METALS CO LTD), 17 December 1996 see abstract; examples 11,17 ---	1-54
Y	US 4 409 043 A (KOON NORMAN C) 11 October 1983 cited in the application see column 2, line 34 - line 36 see column 3, line 42 - line 43 ---	1-54
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 March 1999

Date of mailing of the international search report

12/03/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Ashley, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/21884

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 379 (E-667), 11 October 1988 & JP 63 127505 A (TAIYO YUDEN CO LTD), 31 May 1988 see abstract ---	
A	US 5 314 548 A (PANCHANATHAN VISWANATHAN ET AL) 24 May 1994 ---	
A	EP 0 134 304 A (SUMITOMO SPEC METALS) 20 March 1985 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21884

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 4409043	A 11-10-1983	NONE			
US 5314548	A 24-05-1994	DE 69302329 D			30-05-1996
		DE 69302329 T			19-09-1996
		EP 0576055 A			29-12-1993
		JP 6220502 A			09-08-1994
EP 0134304	A 20-03-1985	JP 1802488 C			26-11-1993
		JP 5010807 B			10-02-1993
		JP 60034005 A			21-02-1985
		CA 1280012 A			12-02-1991
		HK 68690 A			07-09-1990
		JP 2110414 C			21-11-1996
		JP 5112852 A			07-05-1993
		JP 8009752 B			31-01-1996
		JP 1823407 C			10-02-1994
		JP 3170643 A			24-07-1991
		JP 5036495 B			31-05-1993
		US 4859255 A			22-08-1989
		US 5230749 A			27-07-1993